

DETERMINATION OF CHLORINATED INSECTICIDES IN  
BOTTOM SEDIMENT USING AN ELECTRON-CAPTURE GAS  
CHROMATOGRAPHY SCREENING METHOD,  
AUSTIN, TEXAS, 1991 AND 1992

By Robert D. Brock and Lucinda K. Murtagh

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## CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
gram (g)	0.03527	ounce, avoirdupois
kilometer (km)	0.6214	miles
milliliter (mL)	0.0338	ounce, fluid
microliter (μL)	$33.8 \times 10^{-6}$	ounce, fluid

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32.$$

The water-quality abbreviation used in this report is as follows:

microgram per kilogram      (μg/kg)

Other abbreviations used in this report are as follows:

COA-ECSD	City of Austin Environmental and Conservation Services Department
PCB	Polychlorinated biphenyl
PCN	Polychlorinated naphthalene
p,p'-DDD	4,4'- Dichlorodiphenyldichloroethane
p,p'-DDE	4,4'- Dichlorodiphenyldichloroethene
p,p'-DDT	4,4'- Dichlorodiphenyltrichloroethane
USGS	U.S. Geological Survey

# **DETERMINATION OF CHLORINATED INSECTICIDES IN BOTTOM SEDIMENT USING AN ELECTRON-CAPTURE GAS CHROMATOGRAPHY SCREENING METHOD, AUSTIN, TEXAS, 1991 AND 1992**

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## **ABSTRACT**

Twenty-two bottom-sediment samples were collected from Town Lake in Austin, Texas, in 1991 and 1992 and analyzed for chlorinated insecticides by a reconnaissance-quality, electron-capture gas chromatography screening method developed by the U.S. Geological Survey (USGS). Four different chlorinated insecticides (aldrin, chlordane, dieldrin, and p,p'-DDT) and two degradation products of p,p'-DDT (p,p'-DDD and p,p'-DDE) were detected in these samples. The most significant insecticides detected were chlordane, which was detected in 20 of the 22 samples at concentrations that ranged from 26 to 140 micrograms per kilogram, and p,p'-DDT, which was detected in all 22 samples at concentrations that ranged from 5 to 40 micrograms per kilogram. Degradation products of p,p'-DDT were detected in all 22 samples. Concentrations of p,p'-DDD ranged from not detected to 117 micrograms per kilogram and for p,p'-DDE from 9 to 97 micrograms per kilogram. Of the 22 samples collected, 15 also were analyzed by the standard USGS laboratory analytical method for chlorinated insecticides to determine the comparability of the two methods. Correlation coefficients were calculated for chlordane (0.8662), p,p'-DDT (0.6393), p,p'-DDD (0.9401), p,p'-DDE (0.8595), and dieldrin (0.3819). A paired sign test at the 95 percent confidence level showed no significant difference between the screening method and the laboratory analytical method for all detected insecticides except aldrin. P-values were calculated from the data for chlordane (1.0000), p,p'-DDT (0.1796), p,p'-DDD (1.0000), p,p'-DDE (0.1796), and dieldrin (0.2891).

## **INTRODUCTION**

Chlorinated insecticides are highly resistant to chemical and biological transformations and are some of the most persistent anthropogenic compounds introduced in the environment. These compounds are characterized by their relatively small aqueous solubilities and their tendency to partition into sediment organic matter and lipid reservoirs of aquatic organisms. Chlorinated insecticides

may have small dissolved concentrations in water, while their concentrations in sediment can be an order of magnitude greater or more, and their concentrations in aquatic organisms can be as much as a million times greater because of bioconcentration factors (Smith and others, 1988, p. 25-28). Thus, even though many of these compounds are currently (1994) either banned or restricted for private use, they are likely to be present in the sediment, water, and biota of surface-water systems.

The standard USGS laboratory analytical method for determining residues of these insecticides in bottom sediment involves extraction with an organic solvent, concentration, purification using adsorption chromatography, and analysis by gas chromatography with electron-capture detection, using two columns to confirm the identity of the insecticide. This method is time consuming and expensive and may not be appropriate for reconnaissance activities.

In 1991, the U.S. Geological Survey (USGS), in cooperation with the City of Austin Environmental and Conservation Services Department (COA-ECSD), developed a bottom-sediment-screening method for chlorinated insecticides to determine the presence and distribution of these compounds in bottom sediment collected from Town Lake.

### **Purpose and Scope**

The purpose of this report is to present the results from the bottom-sediment-screening method for samples collected from Town Lake in 1991 and 1992 by personnel from the USGS and COA-ECSD. Information concerning the study area, data collection and analysis, and the feasibility of using the screening method as an investigative technique also are included in this report.

### **Description of Study Area**

Town Lake extends through the downtown area of Austin, Texas, for nearly 10 km where the Colorado River is impounded by Longhorn Dam (fig. 1). Its designated uses include public water supply, high-quality aquatic habitat, and contact recreation area for more than 500,000 people in the Austin metropolitan area (Andrews and others, 1988). Eleven different chlorinated insecticides have been reported in the surface-water systems in Austin (Veenhuis and Slade, 1990, p. 45). High levels of impervious cover in the predominantly urban drainage basins associated with Town Lake can transport these compounds to the lake during storm runoff. In a 1987 study (M.O. Hinson, Jr., Hinson & Associates, written commun., 1990) undertaken by a cooperative group of State resource agencies, local and State

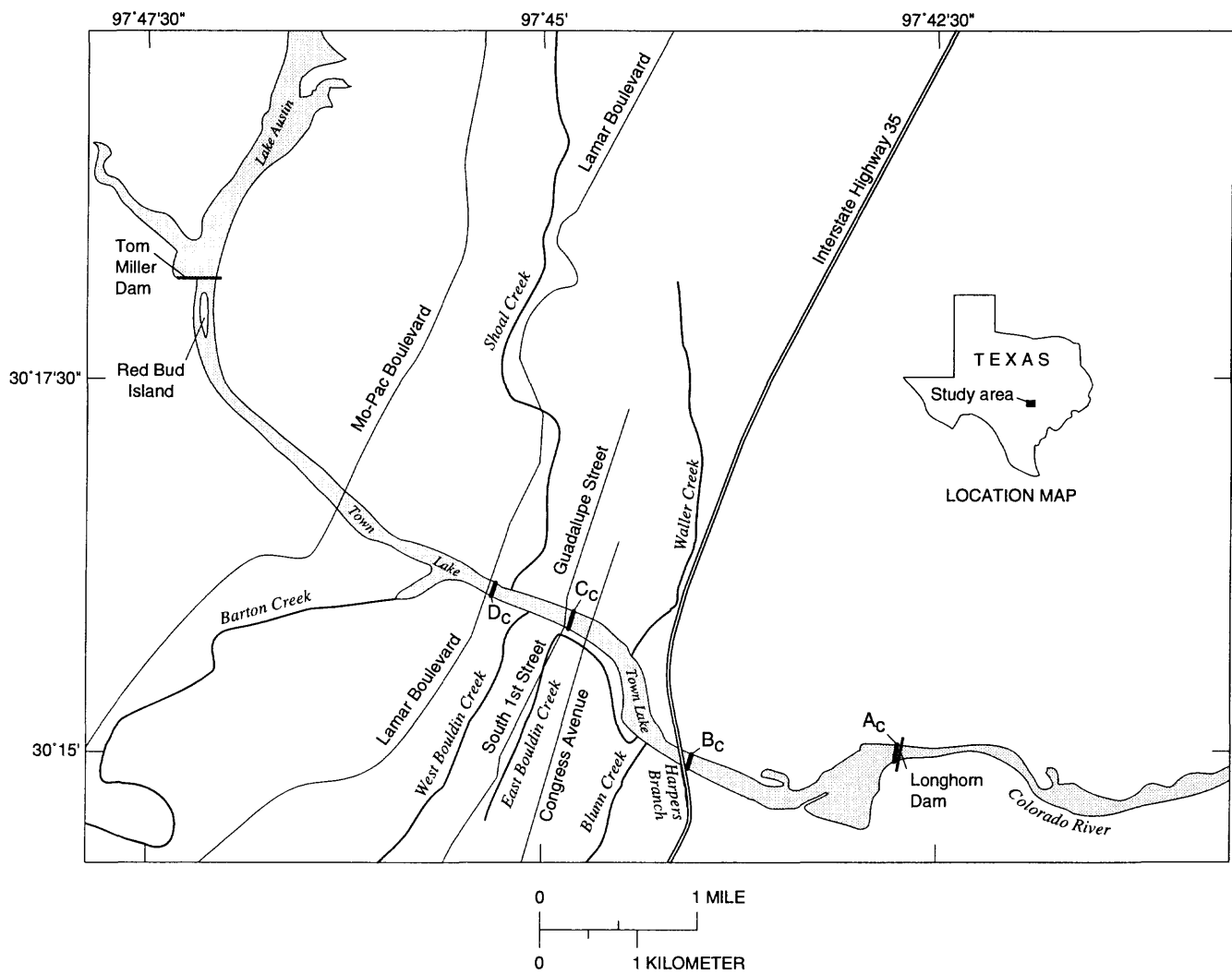


Figure 1.--Location of the study area, Austin, Texas.



health authorities, and public interest organizations, approximately 15 percent of the fish sampled from Town Lake contained chlordane concentrations that exceeded U.S Food and Drug Administration Action Levels (Texas Water Commission, 1990). A fishing advisory that cautions against regular consumption of game fish or consumption of any bottom-feeding fish has been issued.

## **SAMPLE COLLECTION AND ANALYSIS METHODS**

Composite samples, consisting of 5 to 10 point samples, were collected by USGS personnel at six sites in March 1991 and August 1992 using a Ponar grab sampler to provide a representative statistical characterization of the bottom sediment (fig. 1). Point samples also were collected by COA-ECSD personnel at 10 sites in May 1992 using the Ponar grab sampler. The Ponar grab sampler was cleaned prior to collecting each sample with a nonphosphate detergent followed by distilled and native water rinses. Large pieces of debris were removed from the USGS samples prior to compositing, but the samples were not sieved. All samples were chilled to 4°C immediately after collection and stored at 4°C until analysis.

All samples were analyzed by the USGS National Water Quality Laboratory. Fifteen samples were analyzed by both the bottom-sediment-screening method and the standard USGS laboratory analytical method for chlorinated insecticides (Wershaw and others, 1987, p. 31) to determine the comparability of the two methods. The bottom-sediment samples were prepared for screening by weighing out approximately 1 g wet weight of sediment into a 5-mL vial. To the vial were added 1 mL of pesticide-residue-quality methanol and 100 µL of a surrogate solution containing isodrin. The vial then was handshaken for approximately 30 seconds. Then 2 mL of pesticide-residue-quality hexane was added to the vial, and the vial was handshaken for approximately 1 minute. The samples were allowed to stand so that the two solvents would separate. Samples that had emulsions were centrifuged to break the emulsion. The hexane layer was removed from the original vial and placed in another vial containing approximately 0.5 g of mercury and handshaken for approximately 1 minute. The mercury was used to remove sulfur and organosulfur compounds that potentially could interfere with the analysis. At this point, the hexane was ready for analysis by gas chromatography with electron-capture detection.

All samples were analyzed on a Perkin-Elmer gas chromatograph equipped with electron-capture detectors and dual capillary columns (95 percent dimethyl-5 percent diphenyl polysiloxane and 14 percent cyanopropyl-86 percent methyl polysiloxane) (fig. 2). The instrument calibration and operation were the same for the screening method and the laboratory analytical method and followed standard

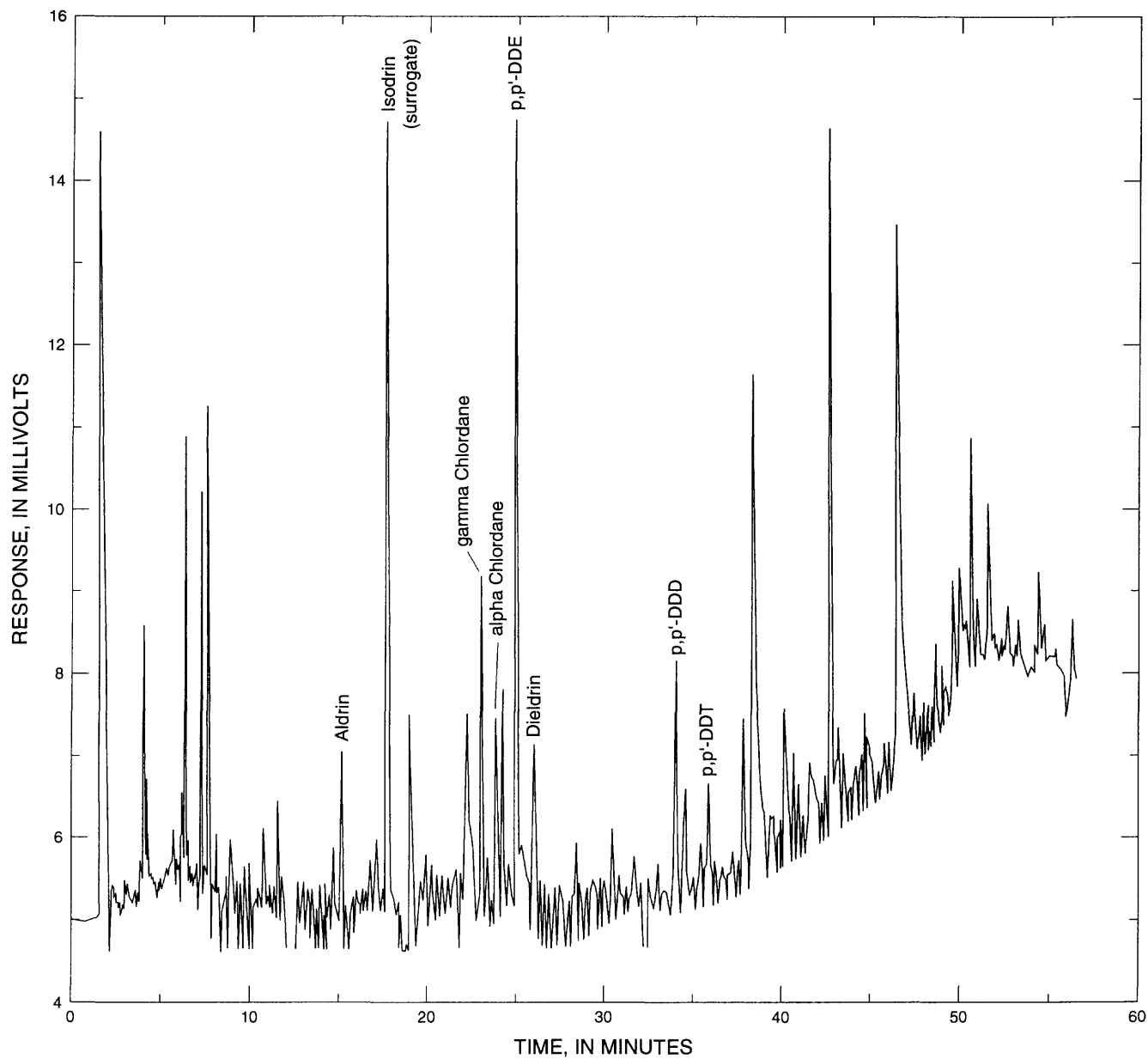


Figure 2.--Screening sample chromatogram from mouth of Shoal Creek at Town Lake, 1992, on a 14 percent cyanopropyl-86 percent methyl polysiloxane capillary column.

USGS laboratory operating procedures. The specific compounds that were determined and their laboratory reporting levels are listed in table 1. These reporting levels may be raised if the compounds are subject to matrix interferences. No attempt was made to determine reporting levels for the screening method.

## RESULTS

Chlorinated insecticides were detected in all bottom-sediment samples collected in 1991 and 1992 (tables 2 and 3). All results are reported on a dry-weight basis. The most significant insecticides detected were chlordane, which was detected in 20 of the 22 screened samples at concentrations that ranged from 26 to 140  $\mu\text{g/kg}$ , and p,p'-DDT, which was detected in all 22 of the screened samples at concentrations that ranged from 5 to 40  $\mu\text{g/kg}$ . Chlordane concentrations were determined from the sum of the alpha and gamma isomers of chlordane from a technical chlordane standard solution. Degradation products of p,p'-DDT were detected in all 22 of the screened samples. Concentrations of p,p'-DDD ranged from not detected to 117  $\mu\text{g/kg}$  and for p,p'-DDE from 9 to 97  $\mu\text{g/kg}$ . Dieldrin was detected in 11 of the screened samples at concentrations that ranged from 2 to 10  $\mu\text{g/kg}$ , and aldrin was detected in 14 of the 22 screened samples at concentrations that ranged from 2 to 12  $\mu\text{g/kg}$ . Gross PCB was detected in 14 of the 15 samples analyzed by the standard USGS laboratory analytical method at concentrations that ranged from 2 to 110  $\mu\text{g/kg}$ . Gross PCB was detected but not quantitated in any of the screened samples.

Graphical comparisons between the screening method and the laboratory analytical method for 15 samples analyzed by both methods for chlordane, p,p'-DDT, p,p'-DDD, p,p'-DDE, and dieldrin are shown in figures 3 through 7. Correlation coefficients (r) were calculated for chlordane (0.8662), p,p'-DDT (0.6393), p,p'-DDD (0.9401), p,p'-DDE (0.8595), and dieldrin (0.3819). Only data pairs that had actual numerical values for both the screening method and the laboratory analytical method are presented graphically (figs. 3-7) and were used for calculating the correlation coefficients. At least 14 data pairs were used to calculate the correlation coefficients for all compounds except dieldrin, which only had 8 data pairs that met these criteria. A correlation coefficient was not calculated for aldrin, which only had three data pairs that met these criteria.

Table 1. -- Specific compounds and reporting levels for compounds included in  
National Water Quality Laboratory schedule 1325

[µg/kg, micrograms per kilogram]

Compound	Reporting level (µg/kg)
Aldrin	0.1
Chlordane	1
p,p'-DDT	.1
p,p'-DDD	.1
p,p'-DDE	.1
Dieldrin	.1
Endosulfan I	.1
Heptachlor	.1
Heptachlor epoxide	.1
Lindane	.1
Methoxychlor	.1
Mirex	.1
Perthane	1
Toxaphene	10
Gross PCB	1
Gross PCN	1

Table 2.--Concentrations of selected chlorinated organic compounds detected in bottom-sediment samples from Town Lake, 1991

[ <, less than; ND, not detected.  
All concentrations in micrograms per kilogram]

Samples collected by U.S. Geological Survey, March 1991						
Compound	Town Lake at site AC		Town Lake at site BC		Town Lake at site CC	
	Laboratory analysis	Screening method	Laboratory analysis	Screening method	Laboratory analysis	Screening method
Aldrin	< 0.1	2	< 0.1	11	< 0.1	ND
Chlordane	32	55	93	76	110	94
p,p'-DDT	5.1	24	38	29	13	22
p,p'-DDD	20	18	53	24	22	14
p,p'-DDE	27	45	< 40	64	42	29
Dieldrin	1.5	2	4.9	4	3.9	3
Gross PCB	17	ND	28	ND	25	ND

Samples collected by U.S. Geological Survey, March 1991						
Compound	Mouth of Shoal Creek at Town Lake		Town Lake at site DC		Town Lake at Mo-Pac Bridge	
	Laboratory analysis	Screening method	Laboratory analysis	Screening method	Laboratory analysis	Screening method
Aldrin	< 10	ND	< 10	8	< 1.0	ND
Chlordane	150	140	32	40	18	28
p,p'-DDT	28	40	3.4	18	5.6	15
p,p'-DDD	37	38	8.8	12	5.8	9
p,p'-DDE	21	48	19	26	12	11
Dieldrin	7.4	8	2.0	4	1.8	ND
Gross PCB	16	ND	9	ND	13	ND

Table 3.--Concentrations of selected chlorinated organic compounds detected in bottom-sediment samples from Town Lake, 1992

[ <, less than; ND, not detected.  
All concentrations in micrograms per kilogram;]  
duplicate results in parentheses]

Samples collected by U.S. Geological Survey, August 1992						
Compound	Town Lake at site AC		Town Lake at site BC		Town Lake at site CC	
	Laboratory analysis	Screening method	Laboratory analysis	Screening method	Laboratory analysis	Screening method
Aldrin	0.1	3 (3)	< 0.1	2	0.5	6
Chlordane	35	46 (35)	40	49	100	74
p,p'-DDT	.3	8 (13)	6.1	10	1.6	13
p,p'-DDD	15	13 (13)	33	32	12	19
p,p'-DDE	25	27 (24)	48	54	31	34
Dieldrin	.7	ND (ND)	.7	ND	1.6	5
Gross PCB	< 3	ND (ND)	10	ND	9	ND

Samples collected by U.S. Geological Survey, August 1992						
Compound	Mouth of Shoal Creek at Town Lake		Town Lake at site DC		Town Lake at Mo-Pac Bridge	
	Laboratory analysis	Screening method	Laboratory analysis	Screening method	Laboratory analysis	Screening method
Aldrin	< 0.1	4	< 0.1	ND	< 0.1	3
Chlordane	61	73	22	30	71	125
p,p'-DDT	< .5	11	41	23	17	9
p,p'-DDD	13	15	< .1	ND	46	66
p,p'-DDE	25	26	11	19	79	97
Dieldrin	1.6	5	.1	ND	.7	ND
Gross PCB	5	ND	2	ND	5	ND

Table 3.--Concentrations of selected chlorinated organic compounds detected in bottom-sediment samples from Town Lake, 1992--Continued

Samples collected by City of Austin, May 1992						
Compound	Longhorn Dam		Town Lake midpoint		Mouth of Shoal Creek at Town Lake	
	Laboratory analysis	Screening method	Laboratory analysis	Screening method	Laboratory analysis	Screening method
Aldrin	< 0.1	3	ND	ND	0.4	6
Chlordane	32	35	35	26	51	45
p,p'-DDT	6.6	7	3.3	6	7.1	6
p,p'-DDD	20	22	130	117	15	15
p,p'-DDE	35	37	37	39	40	31
Dieldrin	.5	ND	.3	ND	1.3	7
Gross PCB	10	ND	110	ND	5	ND

Samples collected by City of Austin, May 1992			
Compound	Harpers Branch	Mouth of Waller Creek at Town Lake	Waller Creek
	Screening method	Screening method	Screening method
Aldrin	ND	12	10
Chlordane	ND	110	54
p,p'-DDT	7	9	13
p,p'-DDD	5	34	14
p,p'-DDE	9	62	28
Dieldrin	ND	ND	10
Gross PCB	ND	ND	ND

Table 3.--Concentrations of selected chlorinated organic compounds detected in bottom-sediment samples from Town Lake, 1992--Continued

Samples collected by City of Austin, May 1992				
Compound	Shoal Creek	Mouth of East Bouldin	Mouth of Barton	Red Bud
	Screening method	Creek at Town Lake Screening method	Creek at Town Lake Screening method	Island Screening method
Aldrin	7	11	ND	ND
Chlordane	60	39	ND	32
p,p'-DDT	5	12	9	12
p,p'-DDD	11	16	11	7
p,p'-DDE	26	25	20	20
Dieldrin	5	4	ND	ND
Gross PCB	ND	ND	ND	ND

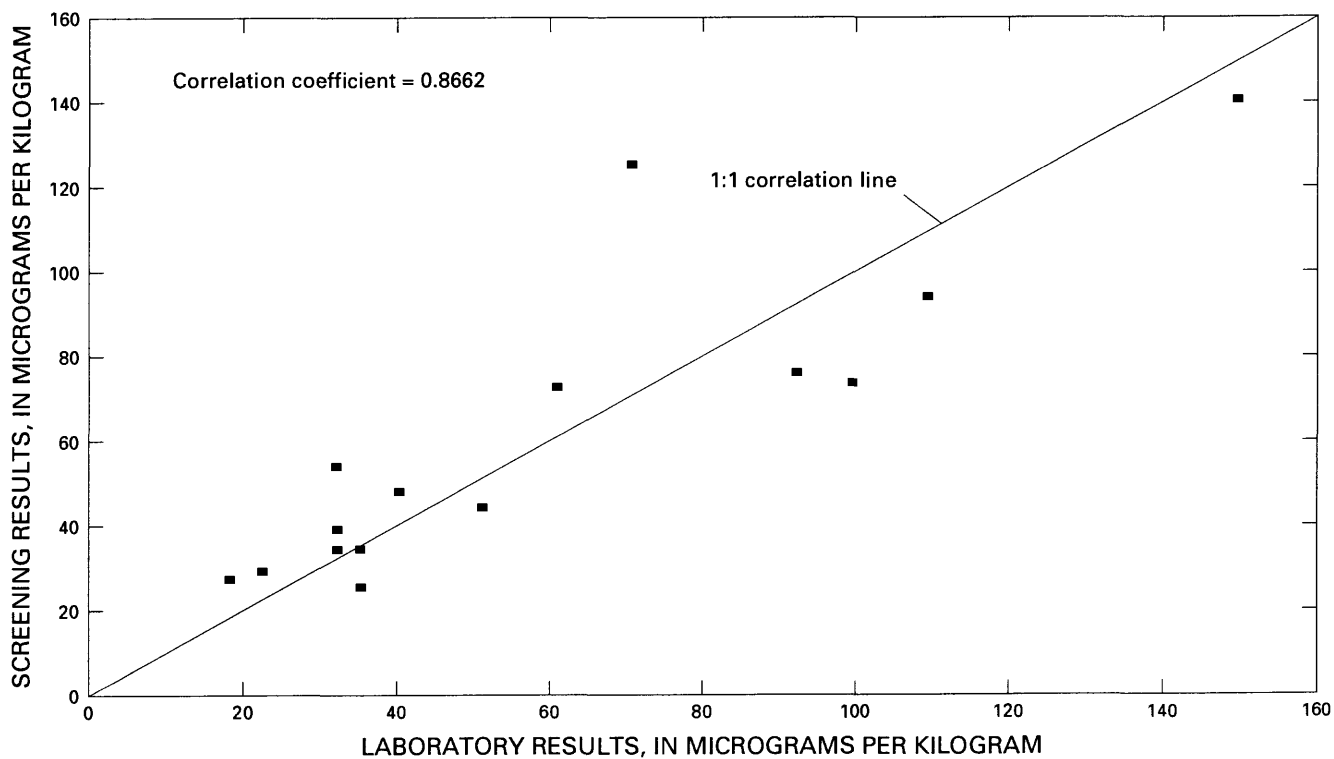


Figure 3.--Correlation between screening method and laboratory analytical method for chlordane.



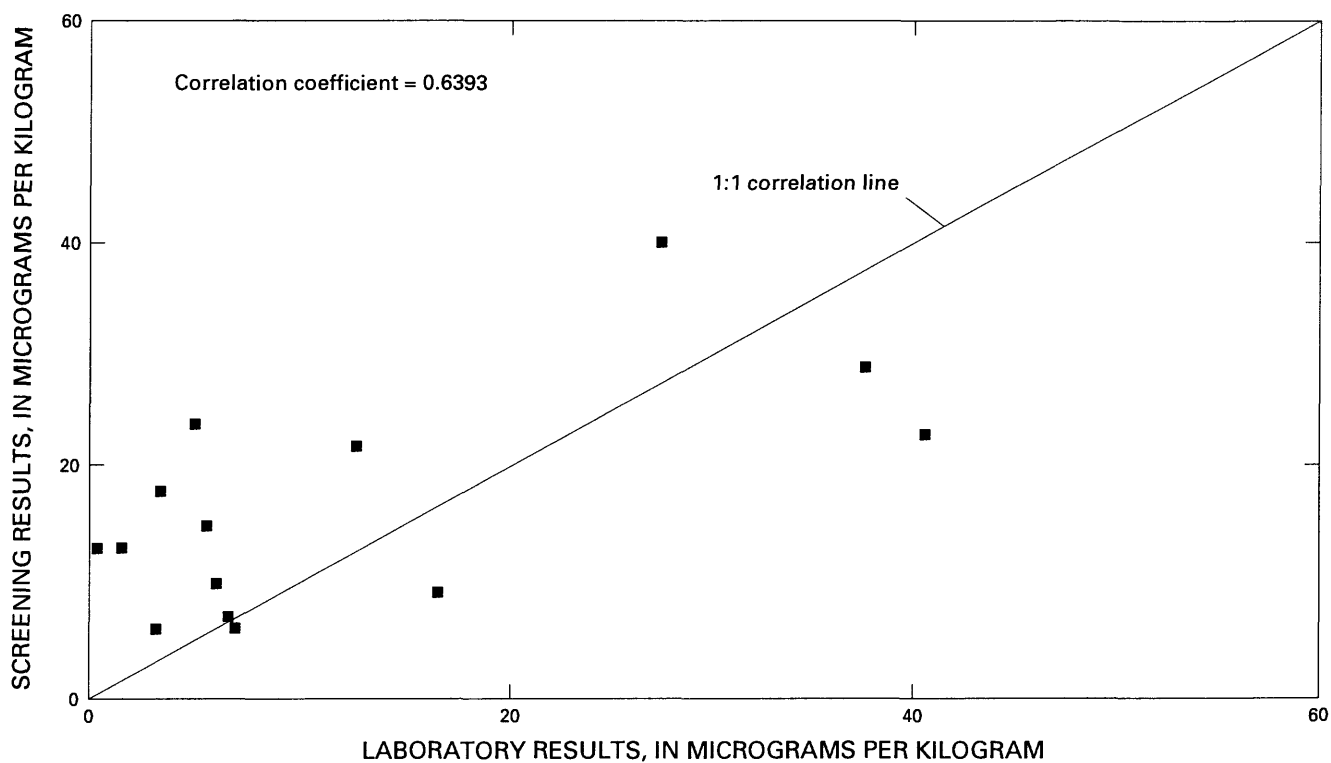


Figure 4.--Correlation between screening method and laboratory analytical method for p,p'-DDT.

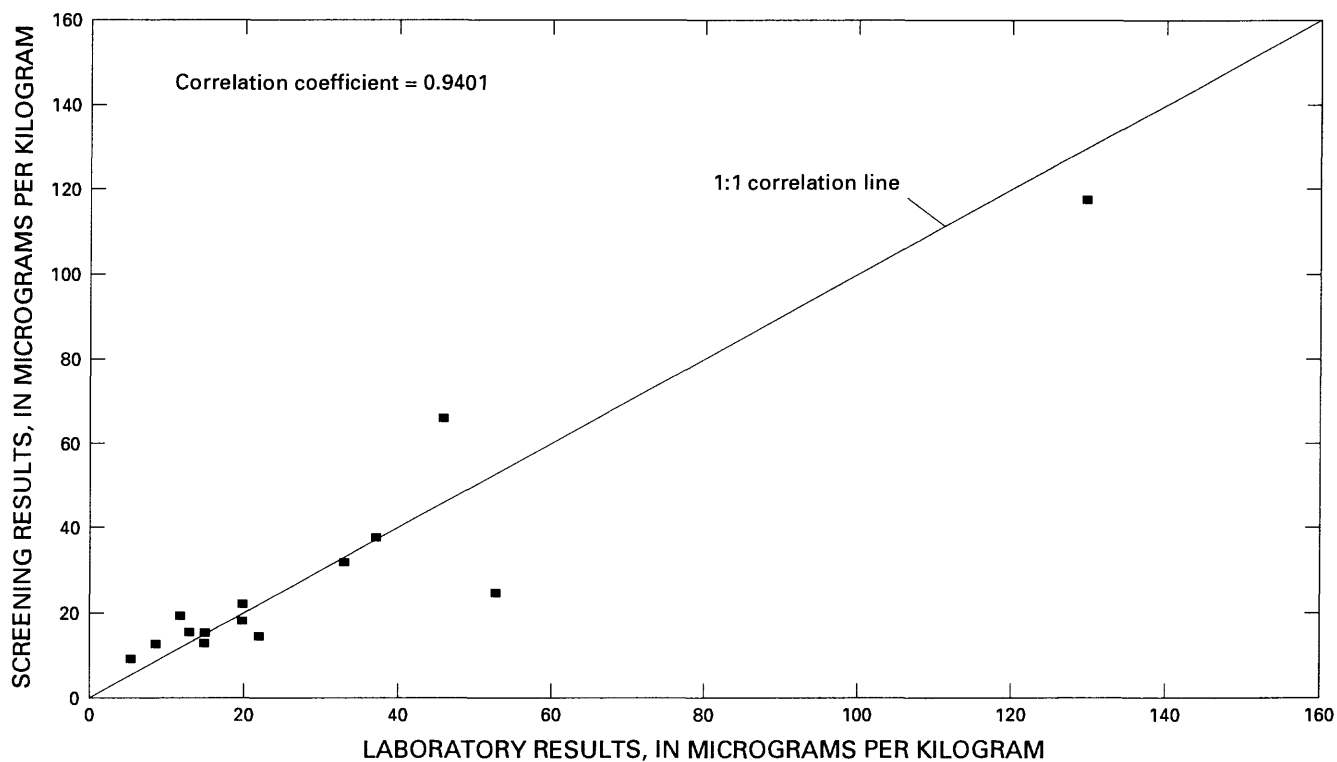


Figure 5.--Correlation between screening method and laboratory analytical method for p,p'-DDD.

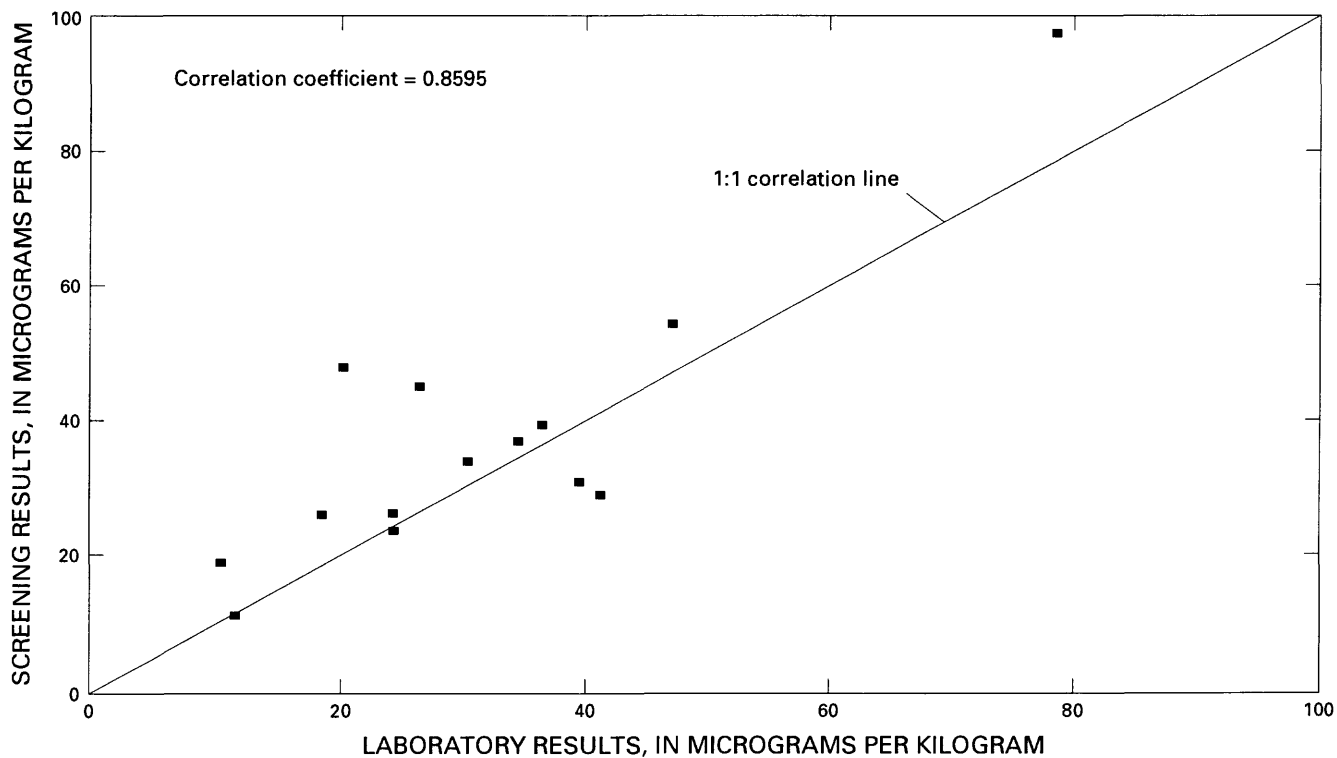


Figure 6.--Correlation between screening method and laboratory analytical method for p,p'-DDE.

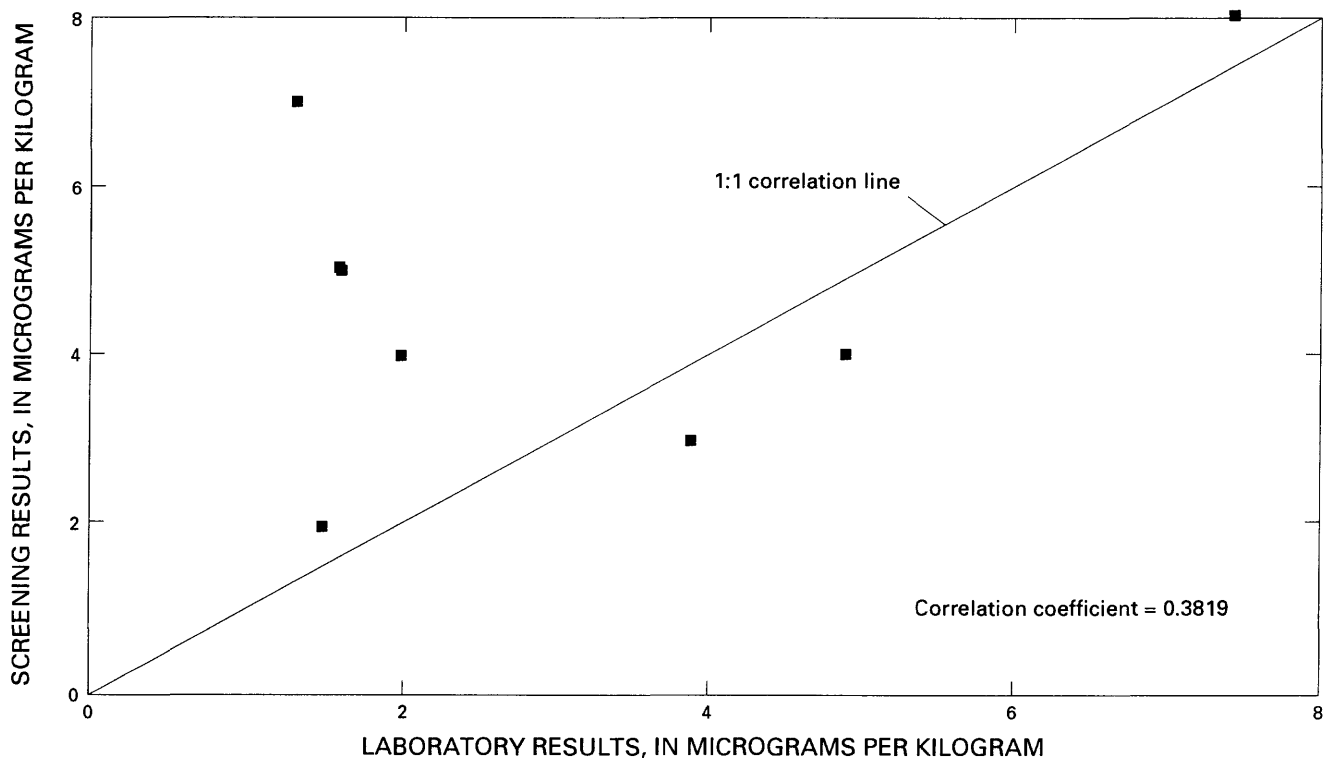
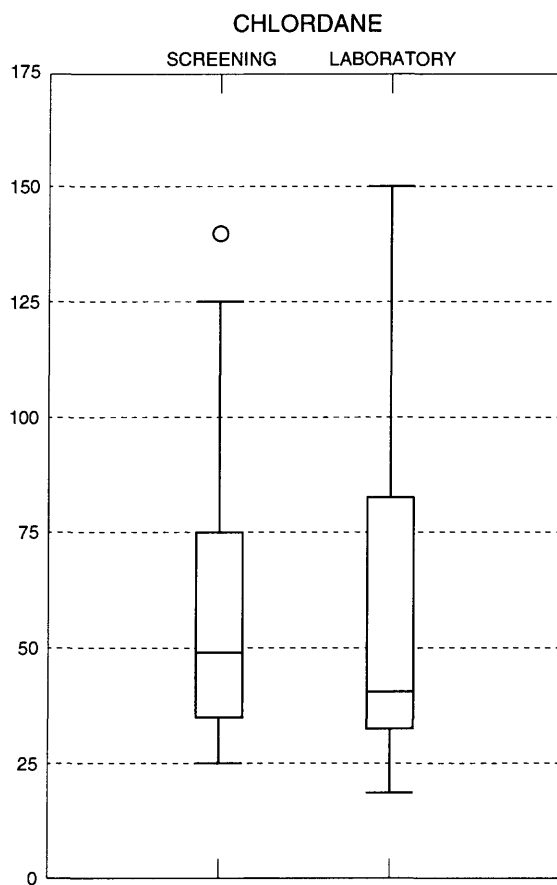


Figure 7.--Correlation between screening method and laboratory analytical method for dieldrin.

False positive values for some compounds of interest could occur in the screened samples because of the presence of chlordane and PCB in the samples, both of which are multicomponent compounds, and because the screened samples were not purified using adsorption chromatography. False positives, relative to the standard laboratory analytical method, do not seem to be a systematic problem for the screened samples except for aldrin. False negative values do not seem to be a systematic problem for the screened samples except when insecticide concentrations are at or near the laboratory reporting level. The size of the sample used for the screening method also could be responsible for some of the differences between the screening method and the laboratory analytical method because of the difficulty in obtaining representative 1-g samples (wet weight) for the screening method as compared to the 100-g samples (wet weight) required for the laboratory analytical method. No attempt was made to determine a reporting level for the screening method, but the results indicate that an estimated reporting level is 10 µg/kg for all detected insecticides. The reporting level for gross PCB was not determined for the screening method either, but it would be substantially higher than the reporting level for the chlorinated insecticides. In general, the screened samples seem to show a positive bias relative to the laboratory samples.

A paired sign test at the 95 percent confidence level (alpha level equals 0.05) was used to compare the screening method results to the standard laboratory analytical method results. The paired sign test was used because it does not require the data to be symmetric or normally distributed. The distributions of these insecticide concentrations are shown in figures 8 through 10. P-values were calculated from the data for chlordane (1.0000), p,p'-DDT (0.1796), p,p'-DDD (1.0000), p,p'-DDE (0.1796), and dieldrin (0.2891). The p-value is a measure of the "believability" of the null hypothesis (Helsel and Hirsch, 1992, p. 108) -- there is no significant difference between the screening method results and the laboratory analytical method results. Since the calculated p-values are greater than the alpha level, the null hypothesis is not rejected for these compounds. The larger the p-value, the stronger the evidence that the data obtained from the two methods are not significantly different. Only data pairs that had actual numerical values for both the screening method and the laboratory analyses were used in the paired sign test. At least 14 data pairs were used to calculate p-values for all compounds except dieldrin, which only had 8 data pairs that met these criteria. P-values were not calculated for aldrin, which only had three data pairs that met these criteria.



#### EXPLANATION

○ DATA VALUES GREATER THAN THE 75TH PERCENTILE PLUS 1.5 TIMES THE INTERQUARTILE RANGE BUT LESS THAN OR EQUAL TO THE 75TH PERCENTILE PLUS 3 TIMES THE INTERQUARTILE RANGE

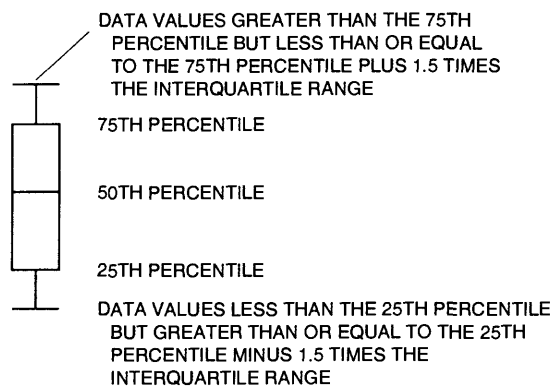
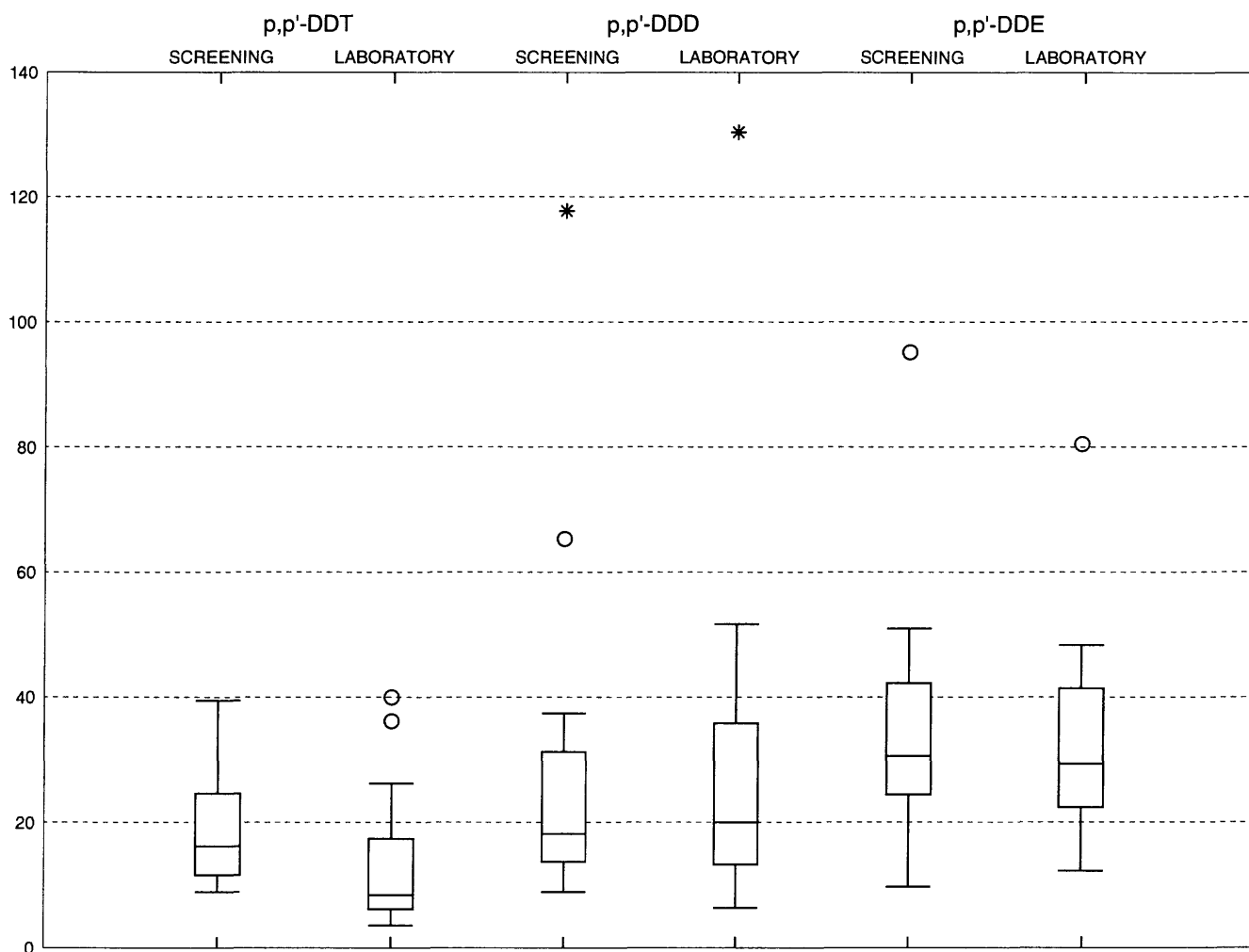


Figure 8.--Distribution of chlordane concentrations for screening method and laboratory analytical method.



#### EXPLANATION

- \* DATA VALUES GREATER THAN THE 75TH PERCENTILE PLUS 3 TIMES THE INTERQUARTILE RANGE
- DATA VALUES GREATER THAN THE 75TH PERCENTILE PLUS 1.5 TIMES THE INTERQUARTILE RANGE BUT LESS THAN OR EQUAL TO THE 75TH PERCENTILE PLUS 3 TIMES THE INTERQUARTILE RANGE

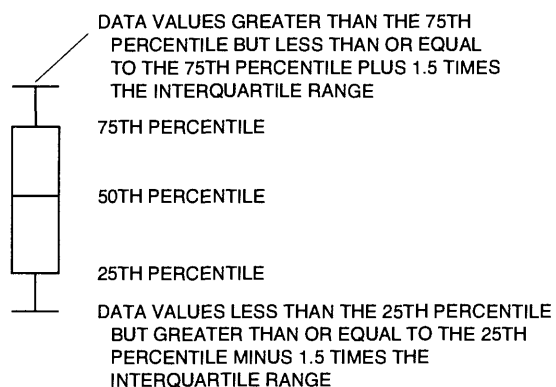


Figure 9.--Distribution of p,p'-DDT, p,p'-DDD, and p,p'-DDE concentrations for screening method and laboratory analytical method.

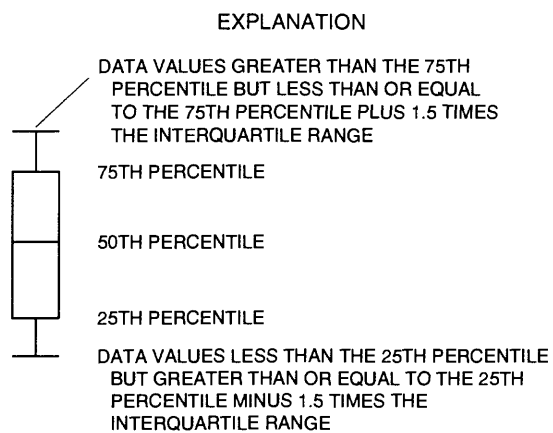
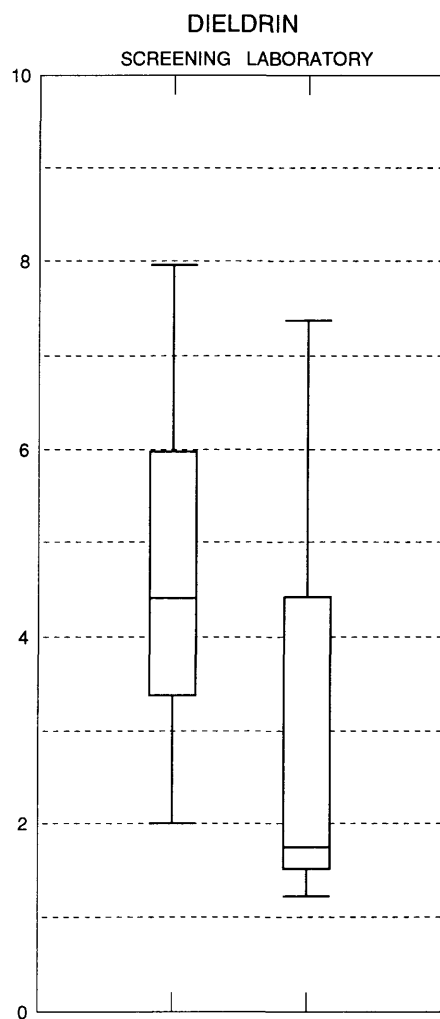


Figure 10.--Distribution of dieldrin concentrations for screening method and laboratory analytical method.

## CONCLUSIONS

Use of the electron-capture gas chromatography screening method was an effective tool that allowed for a thorough determination of the presence and distribution of chlorinated insecticides in samples of bottom sediment from Town Lake. The screening method substantially reduced laboratory costs, which allowed more samples to be analyzed. Chlorinated insecticides were detected in all bottom-sediment samples collected in 1991 and 1992, with chlordane being the most significant insecticide detected. The data from the screening method agree with the laboratory analytical method data and are of sufficient quality for reconnaissance activities. The screening method probably would be applicable for most sediment types and for chlorinated insecticide concentration levels greater than 10 µg/kg. Knowledge of the presence and distribution of these compounds in bottom sediment could be used to design a more effective sampling plan, which could further reduce costs and enable data-quality objectives to be better met.

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